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Equilibrium theory of Quantum fluids via effective pair potential

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Abstract : Using the functional differentiation and topological reduction techniques, we derive effective pair potentials for correlation functions and thermodynamic properties of fluids showing discernible quantum features at low temperature Different properties yield different effective pair potentials and the connection between these potentials is established. These effective pair potentials for the Lennard Jones (LJ) (12-6) potential are shown to be the *modified* L. J. (12 - 6) potential and quantum effects appear through the effective diameter $\tilde{\sigma}$ and the well depth $\tilde{\epsilon}$. Applications are discussed.

Keywords : Quantum fluids, effective pair potentials, correlation functions.

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1 Introduction

The behaviour of matter is fundamentally quantum mechanical. Since quantum effects in most ordinary fluids are negligibly small, classical treatment to obtain their equilibrium properties appears adequate. However, for certain apparently normal fluids, like H_2 and Ne significant deviations from the classical behavior are observed at low temperature. This necessitates inclusion of quantum features in the derivation of their equilibrium properties. One theory envisages that quantum features (excluding these due to the exchange effects) can be included in the calculation equilibrium properties through the effective pair potential (EFP) [1-4]. Furthermore, the EFP may be functions of temperature T and thermal wavelenth λ. However, the EFP is found to be different for different equilibrium properties and no attempt so far has been

made to establish the connection among those. In this paper, we use the cluster expansion and topological reduction techniques to derive the effective pair potentials for the free energy and correlation functions. We then establish inter-relations among them.

2 Basic theory

We consider a D-dimensional quantum fluid (at moderately high temperature) at equilibrium in a volume V and at temperature T. The Helmholtz free energy A of the uniform D-dimensional system can be written as

$$\beta A = N[\ln \rho - 1 + D \ln \lambda] + 1 + H\{\rho, f, f^{III}\} \tag{1}$$

where

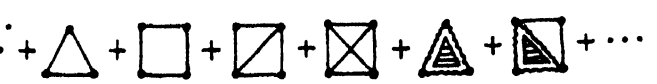
$$f_{ij} = f^c_{ij} + [1 + f^c_{ij}] f^{II}_{ij}$$
$$f^c_{ij} = exp[-\beta u(i,j)] - 1$$

Here u(i, j) is the pair potential between molecules i and j, and f^{II}_{ij} and f^{III}_{ijk} are, respectively, two- and three- body "modified" Mayer functions. In Eq. (1) $\beta = (kT)^{-1}$, $\rho = N/V$ is the number density and H is the excess Helmholtz free energy (relative to the ideal gas at the same temperature and density). H is a functional of the density, ρ and the Mayer functions f and f^{III}. The function H can be used as a generating functional for the direct correlation function, c(1,2) and the radial distribution function (RDF). Furthermore, the cluster expansions for these quantities can be obtained from the cluster expansion of H [1,2].

The diagramatic expansion of H is given by [1]

$$H\{\rho, f, f^{III}\} = G_H \tag{2}$$

where G_H is the sum of all connected irreducible diagrams with no white circles, two or more black ρ circles, at least one f or/and f^{III}-bond and no articulation and nodal circles. The first few diagrams of H are shown as

$G_H =$  $+ \cdots$

Here a solid line represents the f -bond, a curly line indicates (1+f) -link and a shaded triangle the f^{III} -bond. Each black circle has a vertex function ρ

which is integrated over. Elaborate discussions on the diagramatic expansion of G_H can be found in Ref. [1,2]. In our subsequent calculations we write

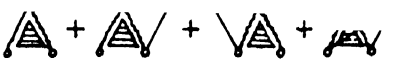
$$G_H = H\{\rho, f, f^{III}\} = H\{\rho, f^{Eff}\} + X \tag{3}$$

f^{Eff} defines an effective Mayer function. X is a set of diagrams of H not included in $H\{\rho, f^{Eff}\}$. $H\{\rho, f^{Eff}\}$ includes all diagrams upto one f^{III} bond and subsets of diagrams with nf^{III}- bonds (n $\geq$ 2). Thus, the diagrams, which are neglected through X, contribute to the higher order quantum correlations.

3 Effective pair potentials for Helmholtz free energy, correlation functions and their relation:

For the calcuation of Helmholtz free energy we introduce an effective Mayer function f^H defined as

$$f_{12}^H = f_{12} + (1 + f_{12})E_{12}^H, \tag{4}$$

where $3E_{12}^H =$  (5)

Eliminating f-bonds in favour of h_o-bonds (where $h_o(i,j) = g_o(i,j) - 1$ is the pair correlation function (PCF) generated by f- bonds) and summing the diagrams of Eq. (5), we get

$$E_{12}^H = (1/3)\int dr_3 f_{123}^{III} g_o(1,2,3)/g_o(1,2) \tag{6}$$

where $g_o(1,2,3)$ is the three - body distribution function generated by f-bond only. The effective pair potential u_H is obtained from this effective Mayer function by the relation

$$u_H(1,2) = u(1,2) - kT\ln[1 + f_{12}^H + E_{12}^H] \approx u(1,2) - kT[f_{12}^H + E_{12}^H] \tag{7}$$

The second expression is obtained for a weak quantum effect. It should be noted further that u_H is a function of density ρ, temperature T and thermal wavelenth λ. It can be used to obtain the internal energy (U) and the pressure (P) as [5]

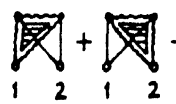
$$U = (3/2)NkT + (1/2)N\rho\int[u_H(1,2) + (\beta\partial u_H(1,2))/\partial\beta]g_H(1,2)dr_2 \tag{8}$$

$$\beta P/\rho = 1 - (1/6)\beta\rho \int [r_{12}\partial u_H(1,2))/\partial r_{12} - 3\rho\partial u_H(1,2)/\partial\rho] g_H(1,2) dr_2 \quad (9)$$

where $g_H(1,2)$ is the RDF generated by f^H. Furthermore, it can be easily shown that $g_H(1,2)$ makes a poor approximation to the actual RDF, g(1,2). To obtain a better approximation for g(1,2) and the correlation function, c(1,2), Sinha and Singh have defined another effective Mayer function as [1,2]

$$f^e_{12} = f_{12} + (1 + f_{12}) E_T(1,2) \quad (10)$$

where $E_T(1,2)$ is a set of elementary diagrams which can yield upon summing

$$\begin{aligned} E_T(1,2) &= \rho \int dr_3 f^{III}_{123} g_o(1,2,3)/g_o(1,2) + O(\rho^2) \\ &= 3E_H(1,2) + [\,\text{  }\,] \end{aligned} \quad (11)$$

The effective pair potential($u^e(1,2)$) in this case is given by the relation

$$u^e(1,2) \approx u(1,2) - kT[f^{II}_{12} + E_T(1,2)] \quad (12)$$

So, different properties lead to different effective pair potentials. To establish the relationship between these potential, we exploit the intimate connection between $g_H(1,2)$ and g(1,2). We can derive by standard procedure

$$g(1,2) = \int g_H(1,3)[\partial \ln(1 + f^H_{13})/\partial \ln(1 + f_{12})] dr_3 \quad (13)$$

Substituting the values of f^H, E_H and g_H in Eq.(13) we get

$$g(1,2) - g_H(1,2) = (2/3)\rho \int dr_3 f^{III}_{123} g_o(1,2,3) + \delta + O(\rho^3) \quad (14)$$

where, $\delta = (2/3)\rho^2 \int dr_3 dr_4 f^{III}_{134} g_o(1,3,4) g_o(1,2)[(4/3)h_o(2,3) + h_o(2,3)h_o(2,4)]$

We thus see that if we know f^H and g_H, we can calculate f^e and $g(1,2)$ or vice versa. Thus we conclude that the effective Mayer function f^e generates the correct RDF at least in the first order of f^{III}, while f^H is suitable for the thermodynamic functions.

4 Effective pair potential for Lennard - Jones (12 - 6) model

In this section we consider a D-dimensional fluid whose molecules interact via the Lennard Jones (LJ) (12-6) potential

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{15}$$

where ϵ represents the well-depth and σ the diameter of the molecule. For such a model, the effective pair potentials $u_H(r)$ and $u_e(r)$ can be expressed in the LJ (12-6) potential forms by simply replacing $\sigma \to \tilde{\sigma}(\alpha)$ and $\epsilon \to \tilde{\epsilon}(\alpha)$ in Eq. (15), where $\alpha = \hbar^2 \beta/2m\sigma^2$. $\tilde{\sigma}$ is the value of r at which $u_H(r)$ or $u_e(r)$ is zero i.e. $u_H(\tilde{\sigma}) = 0$ or $u_e(\tilde{\sigma}) = 0$. Furthermore, the position of the minimum of $u_H(r)$ (or $u_e(r)$) shifts from $2^{1/6}\sigma$ to $2^{1/6}\tilde{\sigma}$, where the effective pair potential is found to be - $\tilde{\epsilon}$. Hence, this relation and Eq.(7) (or Eq.(12)) can be used together to determine $\tilde{\epsilon}$ and $\tilde{\sigma}$. When $\tilde{\sigma}$ and $\tilde{\epsilon}$ are calculated by this procedure, these become functions of D, T, and a quantum parameter π^*. The appearance of the parameter, π^* can be seen by elaborate calculation from α. Thus, the effective pair potentials are expressed as the "modified" LJ(12-6) potential form in terms of $\tilde{\sigma}$ and $\tilde{\epsilon}$.

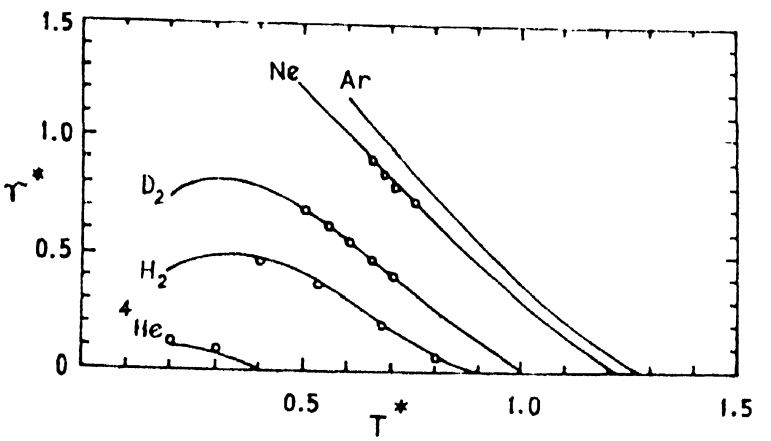


Fig.1 Surface tension γ^* as a function of T^*. Points represent experimental values

As an application of this model, we consider the quantum correlation to the surface tension along the liquid-gas phase boundary. The temperature - dependence of the surface tension of the classical LJ (12-6) fluid is described

by [4]

$$\gamma^* \equiv \gamma\sigma^2/\epsilon = 2.666(1 - T^*/T_c^*)^{1.27} \tag{16}$$

Replacing $\epsilon \to \tilde{\epsilon}$ and $\sigma \to \tilde{\sigma}$, the surface tension of the quantum fluid becomes

$$\tilde{\gamma}^* = 2.666(\hat{\epsilon}/\hat{\sigma}^2)(1 - T^*/1.26\hat{\epsilon})^{1.27} \tag{17}$$

where $T_c^* = 1.26$, $\hat{\sigma} = \tilde{\sigma}/\sigma$ and $\hat{\epsilon} = \tilde{\epsilon}/\epsilon$.

The variation of the surface tension γ^* with respect to temperature T^* for Ne, D_2, H_2 and ^4He is shown in fig.1. along with the experimental results. The qualitative agreement is excellent.

5. Concluding remarks

From the study made in this paper, we find that different effective potentials are obtained for different properties of the system. When the LJ(12-6) potential is used, these effective pair potentials can be expressed in the modified LJ (12-6) potential form by simply replacing $\sigma \to \tilde{\sigma}$ and $\epsilon \to \tilde{\epsilon}$ in Eq.(15) Then the system can be treated classically.

Here we have considered only the first order quantum correction to obtain the effective pair potential. By iterative process the higher order quantum corrections can be included in obtaining the effective pair potential. This will be considered in further publication.

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